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MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11637 as partial fulfillment of the requirements of Project No. 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work was done in the Advanced Propellants Department, Research and Technology Operations, Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1082-81Q-2 and covers the results of work done during the interval 1 November 1966 to 31 January 1967. This project was monitored by Lt. Robert Bargmeyer.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period:

At Aerojet-General

H. Moe, Chemistry Specialist, J. T. Becerril, Senior Laboratory Technician, B. B. White, Manager, Mechanical Properties Laboratory, H. D. Orcutt, Electron Microscopist, W. Hartmann, Hawk Projects.

At Edwards Air Force Base

Lt. R. Bargmeyer

At Hill Air Force Base

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ABSTRACT

The effort on sample acquisition and preparation continued and the analytical phase was well underway. The analytical studies consisted of microscopic studies on selected samples from model grains in accelerated aging and of chemical analyses on a degraded propellant.

The first data obtained from the model grains exceeded expectations. These model grains were made to determine if the microscopic reaction sites could be artificially produced in propellant formulations similar to those in which the microscopic reaction sites were discovered. Small grains were cast and put in storage at various temperatures. When the models were sampled, reaction sites of two basic types were observed in various stages of development. Thus another microscopic procedure is available for interpreting chemical changes during grain aging.

Thin-layer chromatography of ethylene dichloride soluble fractions from degraded propellant showed that at least three different materials are present.

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I. INTRODUCTION

This is the second Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11637. The report covers the period 1 November 1966 to 31 January 1967.

The objectives of this study are to determine the course of the chemical aging process or processes in solid propellant formulations and to define the effects of these degradative chemical processes on the mechanical and ballistic properties of the propellant.

In accordance with these general objectives, the studies have been divided into two phases. The objectives in Phase I are to determine the structure, size and distribution of microscopic reaction sites in solid propellants as a function of age, formulation and storage environments; and to optically characterize and chemically analyze the reaction intermediates and products. In Phase II the mechanistic course of the aging process will be defined.

During the second quarter, work continued on the acquiring of samples from full-scale, field-aged motors, the monitoring of the accelerated aging in model grains, optical microscopic studies, and the initiating of wet chemical studies.

II. PROPELLANT ACQUISITION

A. HAWK MOTOR 15121

Hawk Motor 15121 was described in the previous quarterly report, AFRPL-TR-66-310. A schematic diagram of this motor is shown as Figure 1. Sections 1 through 4 were removed previously and sampled. Section 5 was removed and sampled. This section was of such length so that there is an overlap of the position of propellant samples from motors 15121 and 15062.

Hawk Motor 15121 has been cut down to a size that no longer required the use of manufacturing facilities and was transferred to the R&D facilities. Plans have been made to cut off the fore end-closure in order to determine whether the axial gradient of reaction sites continues for the full length of the grain.

SCHEMATIC OUTLINE OF HAWK GRAIN INDICATING AREAS FROM WHICH PROPELLANT WAS REMOVED

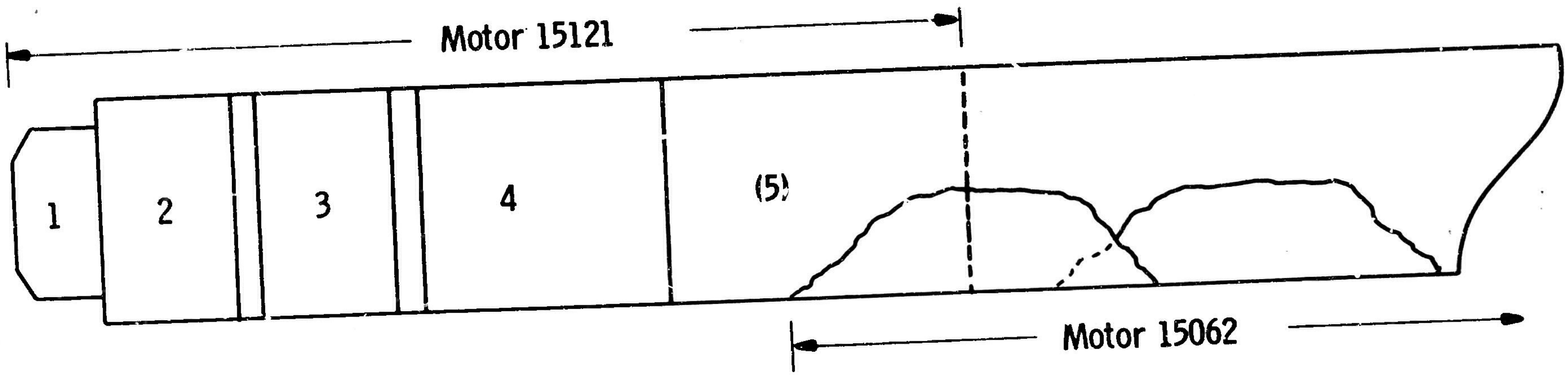


Figure 1

B. MINUTEMAN FIRST STAGE WING I PROPELLANT

An effort is being made, with the help of Lt. Bargmeyer (EAFB) and Mr. Granath (Hill AFB), to obtain samples from a Minuteman First Stage Wing I motor being sectioned by Thiokol Chemical Corp. In arranging for these samples, a diagram showing suggested sample locations was sent to Mr. Granath. The actual sample locations will be reported when the sample and related data are received. The samples are expected at an early date.

C. PREPARATION OF MODEL GRAINS

Two motors of the 3KS-1000 size were prepared with a bipropellant configuration using the Hawk formulation to investigate its accelerated aging characteristics. The propellant in these motors did not cure, but the motors were recast with Hawk propellant from a production batch. These grains were cured and placed in accelerated aging.

III. OPTICAL AND MICROSCOPIC STUDIES

A. MICROSCOPIC REACTION SITES

1. General

Microscopic reaction sites are localized spots in aged propellants with abnormal optical properties when compared to the optical constants of unaged propellants. Prior to the studies under this contract, the reaction sites were partially characterized in field motors during periodic surveillance checks. In these motors the reaction sites were observed to undergo a genesis and after a period of five years, attained their maximum development. The reaction sites in an advanced stage, specifically the five year period, shall serve as a reference for comparison of the model. These reference reaction sites are those observed in a propellant made of polyurethane, NH_4ClO_4, Al and ferric acetylacetonate (FeAA).

2. Description of Reference Reaction Sites

There are two basic types of reaction sites, one characterized by a noticeable change in the refractive index of the propellant, and the other characterized by a series of color absorption shells in the binder. Both reaction sites occur as shells centered about aluminum particles and attain a size that averages about 150 microns. These two types of reaction sites also have characteristically different distributions within the grain. The sites with altered refractive index (refractive sites) attain their maximum development near the bore surface of the grain. The sites with color absorption shell sites (colored sites) occur in bipropellants and attain their most characteristic color pattern near the bipropellant interface. In the bipropellant grains, reaction sites in an intermediate position between the bore and interface may have characteristics common to both basic types.

3. Model Grains-Reaction Site Distribution

The model grains, their storage conditions and relative reaction site content are listed in Table I. In the model bipropellants both type of sites are observed in the booster grain. Advanced stages of colored site formation are numerous while the refractive type are just detectable.

Table I

AGING CONDITIONS AND REACTION SITE DEVELOPMENT IN MODEL GRAINS

Propellant Type	Sample No.	Aging Conditions Time, days	Temp. °F	Relative State of Reaction Site Development Refractive	Color
Igniter	1	89	180	least	-
	2	84	120	intermediate	-
	3	89	110	advanced	-
	4	84	130	intermediate	-
Bipropellant	5	84	150	none	beginning
	6	99	120	beginning	advanced

Comparison of reaction site distribution as a function of aging temperature for the igniter grains shows that the most numerous sites occur at 110°F and the least at 180°F. In the bipropellant, the sample aged at 120°F contains advanced stages of color shell development while in that aged at 150°F reaction site development is less characteristic with diffuse boundaries extending into the binder matrix.

The geometrical distribution of the reaction sites along the grain radius was determined about 1 1/2 inches from the end of the grain. In the igniter grains aged at the three lower temperatures, the sites extend from the bore surface to the Micarta wall with higher concentrations at both surfaces. In the igniter grain aged at the high temperature, small and poorly developed sites occur along the Micarta wall. No reaction sites have appeared at the bore surface. In the bipropellant samples there are a high concentration of colored reaction sites at the interface. Towards the bore surface the colored sites decrease and grade into a lower concentration of the refractive type.

4. Microstructure of Reaction Sites in Model Grains

In the aged model grains, reaction sites in various stages of development are found together. Characteristic features of these sites in the more advanced stages of development are described and illustrated.

a. Refractive Sites

Figures 2a and 2b show the same site in low and in high intensity light. The material around the dark aluminum particle is very clear, colorless and isotropic. The lack of birefringence in this large an area indicates the loss of the micro-atomized NH_4ClO_4 which should be observed in an area of this size. The clear material is composed of two distinct phases, a continuous phase that encloses a discontinuous phase of moderately higher refractive index (Figure 2a). Distributed around the aluminum in the clear continuous phase, as shown in Figure 2b, are numerous small opaque specks that have a red-orange birefringence and exhibit good extinction characteristics.

b. Colored Sites

Figures 2c and d show a diffuse and a condensed site. These two sites are approximately in the same radial position. In a field motor the condensed site would be near the bipropellant interface and would have developed from a red-orange gel phase that is not observed in the model. In Figure 2c, a large central aluminum particle is surrounded by a diffuse, deep gray-green color caused by submicroscopic particles in the binder. The halo has the normal birefringence caused by the contained micro-atomized NH_4ClO_4. There is no indication of a possible NH_4ClO_4 reaction, nor is there any of the altered refractive index material. In Figure 2d, a bright altered refractive index center appears to be enclosed by several opaque particles, which are in turn surrounded by a colored halo. This halo is composed of many translucent green-brown particles with a uniform size of about one micron. This same type of halo is more frequently observed around large single aluminum particles, both variations coexisting in model and field motors, although to a greater extent in the model. The central collection of opaque particles lacks the reflectivity of the aluminum and its composition is unknown.

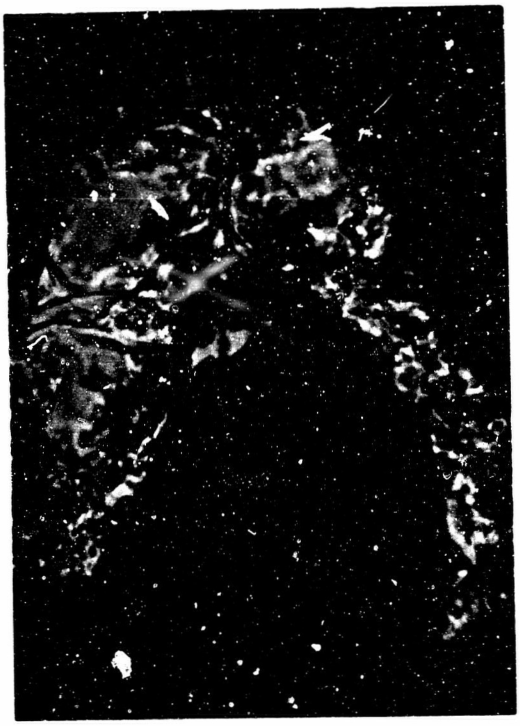
c. Surface Reaction Sites

An odd variation of the refractive site occurs on the surface of the igniter grains as shown in Figures 3a and b. There is an increase in volume of the site so that there is protrusion of the surface skin and eruption.

5. Summary of Reaction Sites in Model Grains

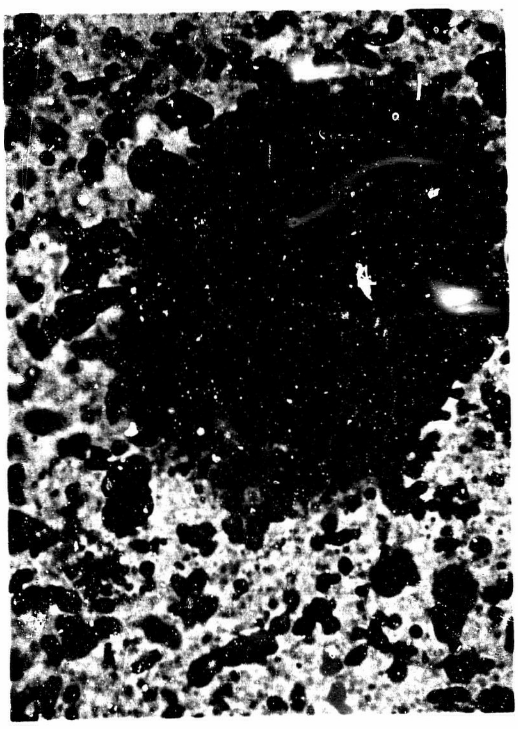
a. Reaction sites have developed in model grains that are similar to the reference reaction sites observed in field motors.

REACTION SITES, REFRACTIVE AND COLORED TYPES
(320 X)



a

b



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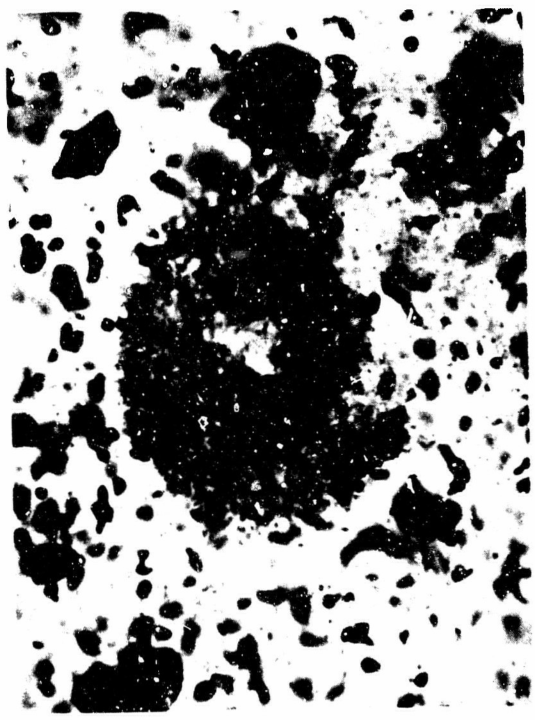
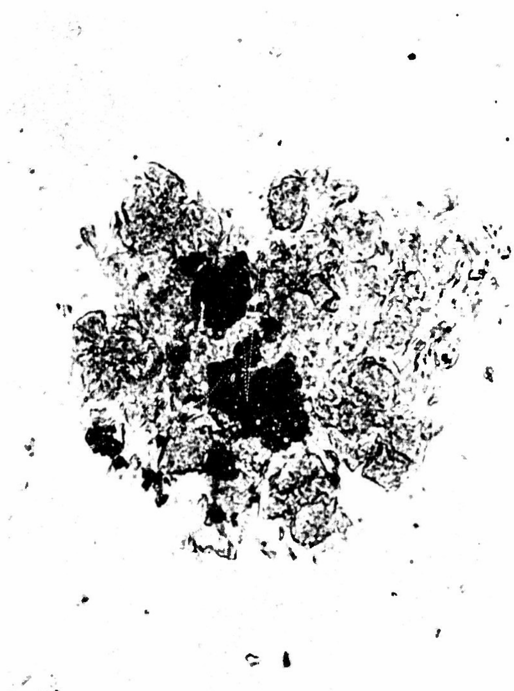


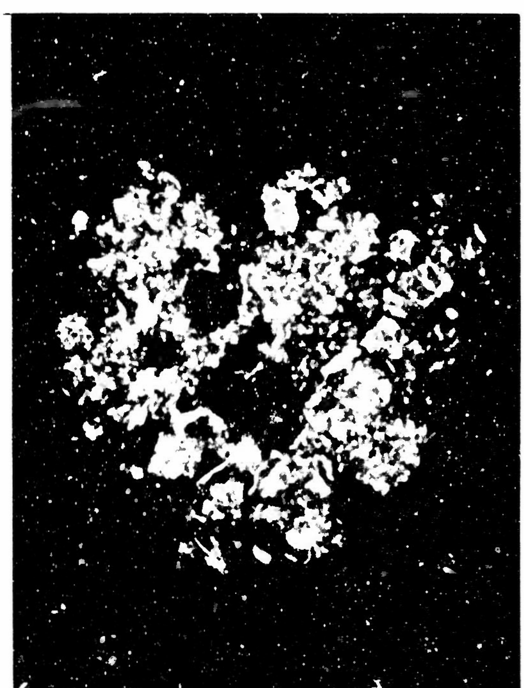
d

Figure 2

REACTION SITES, REFRACTIVE AND BIREFRINGENT

a 210 X b





c 120 X d

Figure 3

b. Temperatures of 110° to 120°F range are more favorable to reaction site formation than higher temperatures. A temperature of 180°F clearly inhibits reaction site formation.

c. Gross characteristics of reaction site distribution patterns in field aged motors are generally maintained in the model grains.

d. Internal characteristics of reaction sites which are typical of their stage of development and their special distribution are less characteristic and tend to commingle in the model grains.

e. The intermediate red-orange gel stage in the development of the colored sites, which is seen in all bipropellant field motors, is missing in the model motors.

B. SEPARATION OF REACTION SITES

Two types of reaction sites of the refractive type were separated from an aged Polaris grain for chemical analysis; one type floated on, and the other settled into ethylene dichloride. The floating reaction site shows a high birefringence and has a polymer spherulite type structure in the halo around the aluminum particle. This led to the conclusion that the reactions occurring in the site had apparently included a bore release compound originally on the bore surface. One of these floating reaction sites is shown in Figure 3c in plane light and in Figure 3d under crossed Nicols where the birefringence is observed.

IV. CHEMICAL ANALYSIS

Two immediate objectives of the chemical analyses are to develop microtechniques and to gather specific chemical data to form a working hypothesis of the aging mechanism. The propellant selected for the initial work is from the Polaris Cycling Unit. This sample contains a surface zone where the entire binder network is degraded plus a high concentration of the refractive type reaction sites. This degraded zone is readily soluble in ethylene dichloride. A sediment and a floating fraction separated which were studied microscopically. The material that went into solution was studied by chromatography.

A 2.8 g sample of degraded binder from the ethylene dichloride soluble fraction was placed upon an 18mm.x 75 cm. alumina column and successively diluted with 300 ml portions of benzene, diethyl ether, and methanol. Evaporation of the eluents gave, respectively: Fraction A, 300 mg.; Fraction B, 300 mg.; and Fraction C, 900 mg. Each of these fractions was redissolved in 10 ml of benzene and the solution used for thin-layer chromatographic analysis.

Silica-gel coated plates were spotted with about 2 lamda (2×10^{-3} ml) of the test solutions. This volume is equivalent to about 0.06 mg. of Fractions A and B, and 0.18 mg. of Fraction C. The spotted plates were developed in separate chambers containing various solvents. The most informative chromatograms are shown in Figure 4. There are at least three components in A and B and two in C. The position of the spots indicate that some of the compounds are in more than one fraction.

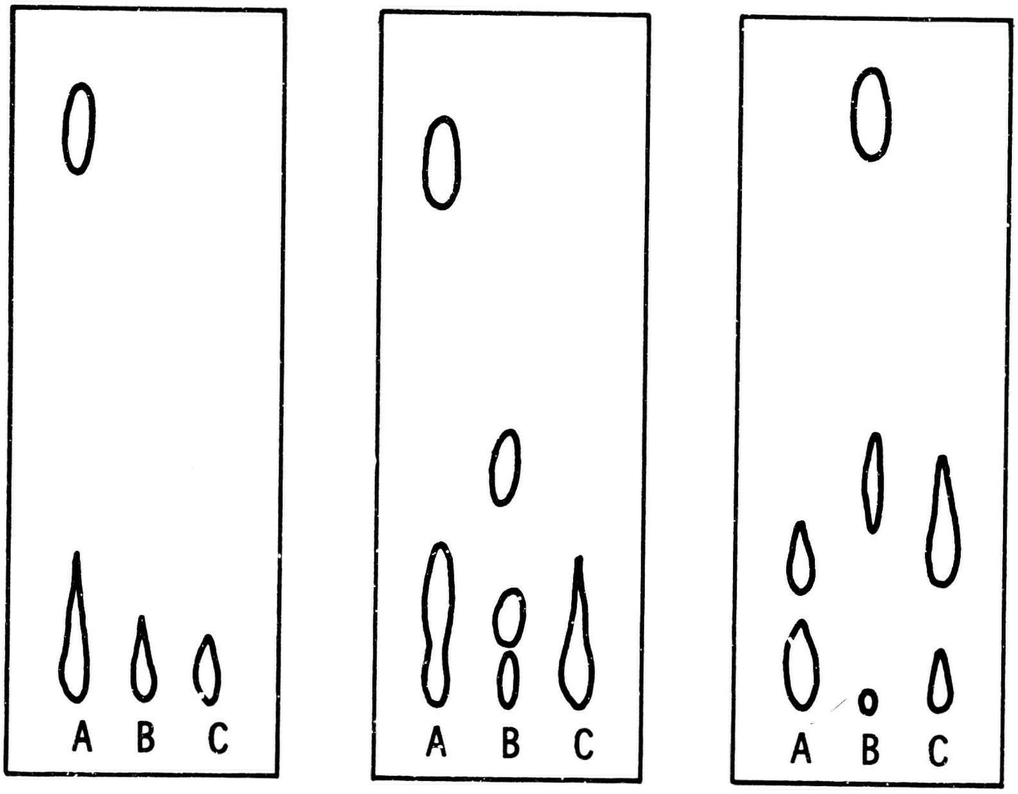
V. CONCLUSIONS

The microscopic changes which occur on aging model grains have similarities to and differences from those which occur in field aged motors. These similarities and differences can be used to gain data concerning propellant aging processes.

VI. FUTURE WORK

During the next quarter the concentrations and distributions of the various type of reaction sites will be determined and compared to those from subsequent sampling periods and from field motors. Chromatographic plates coated with other compounds will be used and attempts made to identify the spotting compound. The chemical technique will be applied to other propellants and the size of the chemical sample will be reduced as techniques are improved.

THIN-LAYER SILICA-GEL CHROMATOGRAPHS OF DEGRADED PROPELLANT (See Text) FRACTIONS



Benzene

Chloroform

Chloroform-Ethanol (15/1)

Figure 4

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